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Pollution Indices as a Tool for the Assessment of Heavy Metals in Soil of Automobile Workshops in Benin City

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Abstract

Soil contamination by heavy metals is increasing day by day. In this study, pollution indices which include geo-accumulation index (I-geo), enrichment factor (EF), environmental risk factor (ERF), contamination factor (CF), degree of contamination (CD), contamination/pollution index (C/PI) and pollution load index (PLI) among others were used. The City was divided into four zones; Northwest (NW), Northeast (NE), Southwest (SW) and Southeast (SE). The average total levels of heavy metals in soil samples analyzed in SE, SW, NE, NW and control were 143.1, 118.6, 129.1, 143.3 and 0.85 mg/kg respectively. The levels of Cd in soils from all the zones were greater than the target values. The results of the I-geo ranged between highly polluted to very highly polluted. The CF showed very high level of contamination for all the heavy metals in all the zones. The C/PI values were less than 1 (contamination range) for all the heavy metals in all zones except for Cd which was greater than 1 (pollution range) in all zones. The negative values of ERF recorded for all the metals in all zones implied that the heavy metals analyzed may present potential environmental threat. The PLI values were 331.08, 313.12, 287.54 and 313.86 for NW, NE, SW and SE respectively. This study revealed that automobile workshop is one of the major sources of anthropogenic soil pollution in Benin City and its environs.

Keywords: Automobile Workshop, Heavy Metals, Pollution Indices and Soil.
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1.0 INTRODUCTION

Soil contamination is an excess of any element or compound through direct or secondary exposure which causes toxic response from biota and/or humans resulting in unacceptable environmental risks (Vangronsveld *et al.* 2009). Contamination of soil with both organic and inorganic compounds is a worldwide problem that has been accentuated by industrialization, urbanization and intensive agriculture. Inorganic pollutants in soil are mainly heavy metals and come essentially from industrial activities: fuel combustion, mineral extraction and processing, vehicular exhaust and particulate emission, coal and fossil fuel combustion metal smelting, etc. Organic pollutants in soil include the listed priority organic pollutants (POPs), chlorinated hydrocarbon pesticides, polychlorobiphenyls, etc. Inorganic and organic pollutants can present a threat to human and ecological health through direct contact or can be a source of contaminant dispersal to groundwater and surface water resources and can hinder the ability of soil to support vegetation and a functioning ecosystem (Martin and Ruby, 2004). In the recent past, there have been increasing interests regarding heavy metal contaminations in the environments, apparently due to their toxicity and perceived persistency within the soil systems (Tijani *et al.* 2005). The most common heavy metals found in the contaminated sites are Cadmium, chromium, copper, lead, mercury, nickel and zinc. These heavy metals are one of the main sources of environmental pollution and affect the human health, life of animals (Mohanty and Mahindrakar, 2011). Heavy metal pollution of soil enhances plant uptake causing accumulation in plant tissues and eventual phytotoxicity and change of plant community (Gimmler *et al.* 2002). In environments with high nutrient levels, metal uptake can be inhibited because of complex formation between nutrient and metal ions (Gothberg *et al.* 2004).Various methods have been employed for the determination of the level of contamination in soils. The most common method is via total elemental analysis (USEPA method 3050) in which the level of contamination is expressed as mg metal kg^{-1} soil. The level of contamination may also be reported as leachable metal and determined by the toxicity characteristic leaching procedure (TCLP) (USEPA method 1311) or the synthetic precipitation leaching procedure (SPLP) (USEPA method 1312). The procedures measure the concentration of metals in leachate from soil contacted with an acetic acid solution (TCLP) or dilute solution of sulphuric acid and nitric acid (SPLP) (DPR-EGASPIN, 2002). This methods gives the total concentration of these metals is soils which passed very little information about the extent and degree of pollution. Thus this research aim at assessing of automechanic soil enriched with heavy metals using indices of pollution. The most common ones are the enrichment factor, environmental risk factor, geoaccumulation index, contamination factor, degree of contamination, pollution load index and contamination/pollution index been widely utilized as a measure of pollution in soil. Total concentrations and fractionation of metals in soil of the automechanic workshops have been documented by Anegbe *et al.* (2018). This study can be considered the first attempt to evaluate the heavy metals pollution in soil of the automechanic workshops in Benin City by using indices of pollution.

2.0 MATERIALS AND METHODS

2.1 Study Area

Benin is a transitory town and a fast growing City with a population of 1,147,188 according to 2006 population census. Benin City is the administrative capital of Edo State. Small-scale enterprises/artisan workshops dot the landscape of the City. Figure 1 shows map with three hundred and thirty-eight sampled automobile workshops. No waste management practice is done on these workshops. Wastes are indiscriminately discarded on the soils.

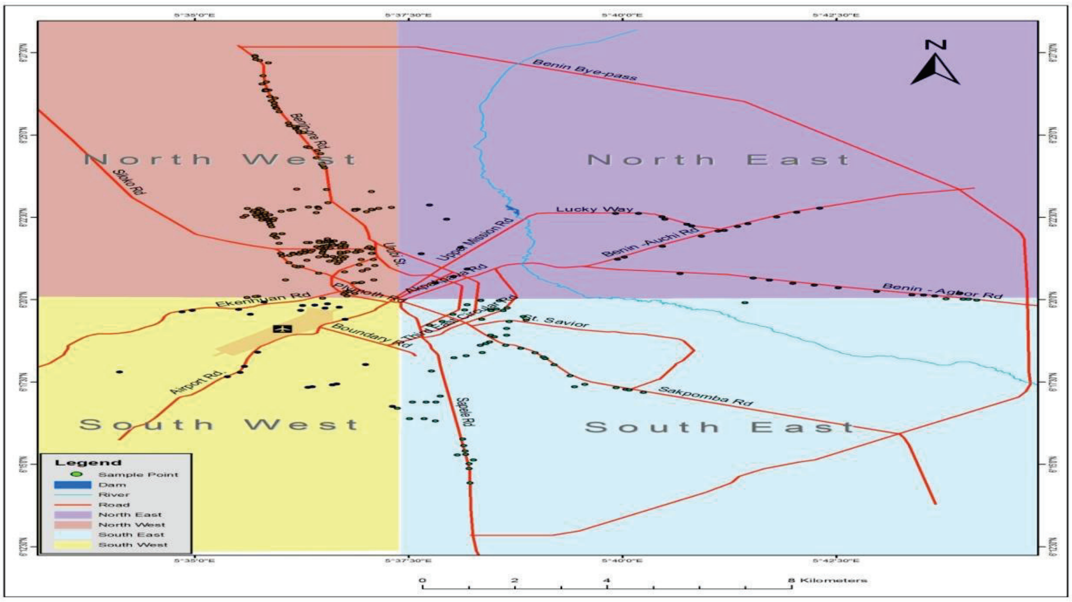

Fig. 1: Map with Three Hundred and Thirty-Eight Sampled Automobile Workshops.

2.2 Soil Sampling Protocol and Preparation

A survey carried out to enumerate automobile workshops in Benin City revealed five hundred and seven (507) active workshops in the metropolis. The City was divided into four zones; Northwest (NW), Northeast (NE), Southwest (SW) and Southeast (SE) to allow a closer examination of the activities within each workshop location in the zones. It was observed that i) a typical automobile workshop accommodated a variety of artisans; mechanics, panel-beater, battery-charger and spray-painter and ii) several semi-automobile workshops operated in clusters each specializing in one-or-more brands of vehicle: cars by brand and/or make, lorries by make etc. It was seldom to find a workshop with lorries and cars. On account of proximity of workshops, activities and duration of operation of the workshops, soil samples were taken from three hundred and thirty-eight (338) workshops. The number of samples to be analysed were further reduced to 40 in the NW zone, 15 in the SE zone, 10 each in the NE and SW zones based on the number of workshops in the zones and the cluster density of workshops in the zones. Top soil samples were collected at the epicentre of the automobile workshop and at a control site farmland in the Faculty of Agriculture, University of Benin. The standard chain of custody for handling soil samples was followed in the transfer of the samples to the laboratory. The soil samples were then air-dried, crushed/ground in a porcelain mortar and sieved through a 2mm mesh. The soil samples with < 2mm size were retained for analysis.

2.3 Determination of the Heavy Metals in Soil Samples

The pseudo-total levels of Ni, Cr, V, Fe, Cd and Pb in soil were extracted by acid digestion in accordance with the USEPA method described by Khodadoust *et al.* (2005). While fractionation was carried out as described by Anegbe *et al*. (2017)

2.4 Soil Pollution Indices

2.4.1 Index of Geoaccumulation (I_{geo})

Index of geoaccumulation (I_{geo}) was used to evaluate the heavy metal pollution by comparing current concentrations with reference (control) values as reported by Bentum *et al.* (2011).

$$\mathbf{I_{geo}} = \mathrm{Log}_2 \frac{Cn}{1.5\ Bn} \quad \text{---------------------------- (1)}$$

2.4.2 Environmental Risk Factor
It is assessed from the fractionation of heavy metals to determine the labile and recalcitrant metal pools in the soil using the expression (Saenz *et al*. 2003; Lin *et al*. 2006)

$$ERF = \frac{CSQV - C_i}{CSQV} \quad --------(2)$$

Where CSQV= Concentration of the soil quality value (heavy metal concentration in residual fraction of the soil (assumed to be equivalent to the background/pre-industrial concentration).
Ci = heavy metal concentration in the first three fractions in the soil.

2.4.3 Enrichment Factor
The extent of soils contamination was assessed using the enrichment factor (EF) (Woitke, 2003; Reddy, *et al.* 2004; Selvaraj, *et al.* 2004). It has also been used to indicate the degree of pollution or contamination or both. Data from samples taken from the control site was used to establish metal-normalizer relationships to which the data generated from various mechanic workshops are compared. According to this technique, metal concentrations were normalized to the textural characteristic of soils. Most commonly used reference elements include Sc, Mn, Al and Fe, (Loska*et al*. 1997). In this study, Fe was chosen as the geochemical normalizer because of its conservative nature during diagenesis, (Chapman and Wang, 2001). Moreover, soils in Nigeria have been reported to be rich in Fe. Based on Rubio *et al*. (2000), EF is defined as:

$$EF = \frac{\frac{X}{Fe}_{soil}}{\frac{X}{Fe}_{earth\text{'}s crust}} \quad ----------------(3)$$

Where (X/Fe)soil is the ratio of heavy metal (X) to Fe in the soil from mechanic workshops, and (X/Fe)background is the natural background value of the Metal-Fe ratio.

2.4.4 Contamination Factor
Contamination factor (CF) is given by the ratio of the pseudo-total level of the contaminant by the test soil sample to the level in the background sample and indicated on a contamination factor scale of 1-6 viz: CF < 1, low level of contamination, 1≤ CF < 3, moderate level of contamination, 3 < CF < 6, considerable level of contamination, and CF > 6, very high level of contamination (Hakanson, 1980; Anegbe *et al*. 2017).

$$CF = \frac{\text{Cm Sample}}{\text{Cm Background}} \text{----------------------------(4)}$$

Cm Sample = metal concentration in Sample
Cm Background = metal concentration in background or control Sample. (Lin *et al.* 2009)

2.4.5 Contamination/Pollution Index
Contamination/pollution (C/P) index provides assessment of the extent of enrichment of test soil/site above the target regulatory values and is given by the ratio of the level of the contaminant in the test soil sample to the target value,

$$C/PI = \frac{\text{Concentration of metal in soil}}{\text{Target value from reference table}} \text{------------(5)}$$

2.4.6 Degree of Contamination
The sum of contamination factors for all elements examined represents the contamination degree (CD) of the environment and four classes are recognized (Table10).

2.4.7 Pollution Load Index (PLI)
Generally, pollution load index (PLI) as reported by Harikumar *et al.* (2009), is as follows:

$$PLI = \sqrt[n]{Cf1 \ x \ Cf2 \ x \ Cf3 \ x \ Cf4 \ \dots\dots\dots\dots\dots\dots Cfn} \text{----------------------------------(6)}$$

Where, CF = contamination factor, n = number of metals

3.0 Results and Discussion

3.1 Comparison of average total levels of heavy metals in soil samples of automobile workshops in Benin City with levels in control soil sample
Comparison of the pseudo-total levels of heavy metals in contaminated soil with the levels in uncontaminated (control soil) may provide a first-tier indication of “enrichment” of heavy metals in contaminated soil. Though of limited value, a direct comparison of the levels of heavy metals in the control soil sample with the levels in soil samples from automobile workshops in Benin City is given in Table 1.

Table 1:Comparison of Average Total Levels of Heavy Metals in Soil Samples from Automobile Workshops in Benin City with Levels in Control Soil Samples

Location/Zone	$M_{Total.}$ (mg.kg^{-1})
SE	143.1
SW	118.6
NE	129.1
NW	143.3
Control	0.85

These results show that the levels of heavy metals in soil samples from the automobile workshops were several orders of magnitude higher than the levels in the control soil sample, suggesting a deleterious impact of activities in automobile workshops on soil quality in Benin City.

3.2 Comparison of Average Total Levels of Heavy Metals in Soil Samples Automobile Workshops in Benin City with Target and Intervention Values

Two parameters have been defined by the local Environmental Regulatory Agencies for contaminated soil: the intervention value and the target value. Intervention values indicate the quality for which the functionality of soil for human, animal and plant lives is considered threatened by the contaminant. The values are related to soil properties: soil organic matter and clay contents and therefore site specific. The values may be obtained by using the relationship

$$Ie = \frac{(Ist\,.\,A) + (B\,.\,\%clay) + C\,.\,\%OM)}{A + 25B + 10C} \quad \text{----------------------------------(7)}$$

where Ie = intervention value (mg.kg^{-1})
Ist = intervention value of standard soil (mg.kg^{-1})
% clay = measured clay content of test soil sample
% OM = measured organic content of test soil sample
A, B and C are constants that depend on the metal contaminant

Target values (M_{Target}) indicate the soil quality with respect to a contaminant required for sustainability or expressed in terms of remedial policy, as the soil quality required for the full restoration of soil's functionality for human, animal and plant life. Target values are therefore the benchmark against which soil and/or site remediation endpoint may be compared and/or assessed.

Table 2: Comparison of Average Total Levels of Heavy Metals in Soil Samples from Automobile Workshops in Benin City with Target and Intervention Values.

Heavy Metals	$M_{(Target)}$* (mg.kg^{-1})	$M_{(Intervention)}$* (mg.kg^{-1})	Average total levels of heavy metals in test soils samples (mg.kg^{-1}) from automobile workshops			
			NW zone	SE zone	NE zone	SW zone
Cd	0.8	12	6.7	6.9	6.5	6.0
Cr	100	380	49.0	49.0	40.80	37.70
Ni	35	210	27.6	26.9	27.10	25.30
Pb	85	530	28.1	26.7	25.60	24.10

** Dutch Environmental Quality Standards.*

The results given in table 2 compare the average total levels of the heavy metals in soil samples from automobile workshops in Benin City with the target and intervention values. It could be observed that all the heavy metals analyzed except cadmium have average total levels less than their target values, hence may be considered to present no environmental concern. It was also observed that all the individual metal analyzed in all the zones showed average total concentration that were below their intervention values. There was no target and intervention values for vanadium.

3.3 Index of Geoaccumulation (I_{geo})

As reported in table 3, this index consists of seven scales (0–6) ranging from unpolluted to very highly polluted. The interpretation of the results was made based on the scale above in comparison with control sample.

Table 3: Geoaccumulation Indices for Sediment (Soil) Quality (Singh *et al*. 2003)

I_{geo}	Class	Sediment (soil) quality
0	0	Unpolluted
0-1	1	unpolluted to moderately polluted
1-2	2	moderately polluted
2-3	3	moderately-to-highly polluted
3-4	4	highly polluted
4-5	5	highly-to-very highly polluted
> 5	6	very highly polluted

From the I_{geo} values (Table 4), the soils in automobile workshops may be said to be highly to very highly polluted, reflecting a higher degree of pollution than soils from the Ikhueniro open dump site in Benin (Ataikiru and Okieimen, 2014).

Table 4: I_{geo}Values for Soil Samples from Automobile Workshops in Benin City

Zone of workshop	Heavy metals	I_{geo} values	Status of pollution
NW	Cd	6.10	very highly polluted
	Cr	4.90	highly-to-very highly polluted
	Pb	4.07	highly-to-very highly polluted
	Ni	4.10	highly-to-very highly polluted
	V	7.71	very highly polluted
NE	Cd	6.07	very highly polluted
	Cr	4.82	highly-to-very highly polluted
	Pb	3.98	highly polluted
	Ni	4.17	highly-to-very highly polluted
	V	7.57	very highly polluted
SW	Cd	5.99	highly polluted
	Cr	4.70	highly-to-very highly polluted
	Pb	3.92	highly polluted
	Ni	4.06	highly-to-very highly polluted
	V	7.44	very highly polluted
SE	Cd	6.13	very highly polluted
	Cr	5.00	highly-to-very highly polluted
	Pb	4.01	highly polluted
	Ni	4.12	highly-to-very highly polluted
	V	7.71	very highly polluted

3.4 Environmental Risk Factor

The environmental risk factor (ERF) is a pollution index used to determine environmental risk and establish potential threat of heavy metals organisms in the environment.

ERF < 0 = potential environmental threat

ERF > 0 = no potential environmental threat

Table 5:Environmental Risk Factors of Heavy Metals inSoils from Automobile Workshops in Benin City

Heavy metal	Zone/ERF values			
	NW	SE	NE	SW
Cd	-3.02	-2.76	-2.55	-2.77
Fe	-3.18	-2.33	-3.59	-3.56
Pb	-1.62	-2.01	-1.24	-1.22
Ni	-2.17	-2.31	-2.97	-3.18
V	-2.68	-2.92	-3.57	-3.31
Cr	-2.53	-2.97	-3.81	-2.80

The ERF values obtained for soil samples from automobile workshops in Benin City (Table 5) are below 0 and indicate that the heavy metals in the soils samples from the automobile workshops present potential environmental threat.

3.5 Enrichment Factor

EF was used in the study to assess the relative contributions of natural and anthropogenic heavy metal inputs to soils (Adamo, *et al*. 2005).

The EF values close to unity indicates crusted origin, those less than 1.0 suggest a possible mobilization or depletion of metals, whereas EF > 1.0 indicates that the element is of anthropogenic origin.

Five contamination categories are recognized and interpreted as suggested by Birth (2003);

EF < 1 indicates no enrichment, EF < 3 is minor enrichment, EF = 3 - 5 is moderate enrichment, EF = 5 - 10 is moderately severe enrichment, EF = 10 - 25 is severe enrichment, EF = 25 - 50 is very severe enrichment and EF > 50 is extremely severe enrichment. Details of the EF values of the metals studied in all the zones (NE, SE, NW and SW) with respect to the natural background concentration are presented in Table 6. Apart from Cd and V whose EF factors value were 0, i.e less than 1.0 suggesting a possible mobilization or depletion of metals, others (Cr, Pb and Ni) has EF > 1.0 clearly indicate that the elements are of anthropogenic origin.

In general, there was no much variation in the EFs of Pb, Cr and Ni in all zones under investigation.

The enrichment factor of Ni, Pb and Cr in all the zones as shown in table 6. 19-3.22 ranged from; minor enrichment to severe enrichment. (EF < 3 to EF = 10 – 25). No site in all the zones recorded a value of EF = 25 – 50 and EF > 50 which means there is no case of very severe enrichment and extremely severe enrichment of metals in all the auto-mechanic workshops.

In a recent report, it has been shown that high EFs do not provide a reliable indication of the degree of human interference with the global environment (Sucharovà *et al*. 2012). In the report carried out in Czech Republic, where five different elements were used as reference, the sequence of the EFs do not reflect the relative importance of the elements determined. It was concluded that other factors such as the choice of reference element may be responsible for high EFs. The slight variation in EFs from site to site may also reflect the age of establishment of the various workshops and indicative of the number of services each workshops render.

Table 6: Enrichment Factor of Heavy Metals in Soil Samples from Automobile Workshops in Benin City

Heavy metals	Crustal abundance* ($mg.kg^{-1}$)	Location of workshop/ Enrichment factor			
		NW	NE	SW	SE
Cd	0.15	18.72	18.16	16.76	19.27
Cr	102	6.22	5.18	4.79	6.25
Pb	14	2.45	2.23	2.10	2.33
Ni	84	2.66	2.61	2.45	2.59
V		89.08	93.29	71.22	93.29

**The crustal abundance of selected elements.*

3.6 Contamination Factor

From the results of the contamination factors shown above, all the zones showed very high level of contamination with respect to all the heavy metals analyzed. This might be attributed to the very concentrations of the heavy metals in the automobile workshop sites compare to their respective concentrations in the control.

Table 7: Contamination Factors of the Heavy Metals from Automobile Workshops in Benin City

Heavy metals	CF			
	NW	NE	SW	SE
Cd	670	650.00	600.00	690.00
Cr	222.73	185.45	171.36	223.64
Pb	87.81	80.00	75.31	83.44
Ni	95.17	93.45	87.24	92.76
V	3190.0	3340.0	2910	2550

3.7 Contamination/Pollution Index

A distinction between soil contamination and pollution range was established by means of the contamination/pollution index C/PI (Table 8). C/P index values greater than unity (1) defines the pollution range, and when lowers than unity defines the contamination range. The standard employed for interpreting soil heavy metals contamination/pollution index varies from country to country based on the chosen factors (Lacatusu, 2000).

Table 8: C/PI Significance

C/PI	Significance
< 0.1	Very slight contamination
0.10-0.25	Slight contamination
0.26-0.50	Moderate contamination
0.51-0.75	Severe contamination
0.76-1.00	Very severe contamination
1.10-2.00	Slight pollution
2.10-4.00	Moderate pollution
4.10-8.00	Severe pollution
8.10-16.00	Very severe pollution
>16.00	Excessive pollution

Table 9: C/P Index of the Heavy Metals from Automobile Workshops in Benin City

Heavy metals	C/P index			
	NW	NE	SW	SE
Cd	8.38	8.13	7.50	8.63
Cr	0.49	0.41	0.38	0.49
Pb	0.33	0.30	0.28	0.31
Ni	0.79	0.77	0.72	0.77
V	-	-	-	-

Table 10: Classes of Contamination Degree (CD) (Hakanson, 1980).

Classes	Contamination Degree (CD)
Cdeg < 8	Low degree of contamination
8 < Cdeg < 16	Moderate degree of contamination
16 < Cdeg < 32	Considerable degree of contamination
Cdeg >32	Very high degree of contamination

The values of the C/P index of the heavy metals from automobile workshops in Benin City are given in Table 9. Using the C/P index, the soil samples may be classified as moderately contaminated with respect to Pb and Cr in all the zones, very severely contaminated with respect to Ni in all zones except in SW zone where it showed severe contamination, and Very severely polluted with respect to Cd in all the zones except in SW zone where it showed severe pollution.

3.8 Degree of Contamination

The contamination factor described in Table 7 is a single element index. The sums of contamination factors for all the metals examined are listed in Table11.

Using the sum of contamination factors obtained in Table7 for all elements in each zone, the contamination degree (CD) for each zone is therefore calculated as shown in Table 11 below: From Table 11, the degree of contamination (CD) values for all the zones are greater than 32. Hence, the soils in the vicinity of the automobile workshops in all the zones are therefore classified as having very high degree of contamination. However, it is worthy of note that soil samples from NE zone has the highest degree of contamination compare to other zones. The highest degree of contamination observed in the NE zone may be attributed to the large size and old age of many of automobile workshops in the zone coupled with the location of the zone within Benin City metropolis, and high volume of wastes deposited at those workshops found within the zone.

3.9 Pollution Load Index (PLI)

PLI provides a rather simple means of assessing soil/site quality.

The PLI value of > 1 is polluted, whereas < 1 indicates no pollution (Harikumar *et al.* 2009*)*.

Table 11:Contamination Degree and Pollution Load Index ofHeavy Metals inSoil Samples from Automobile Workshops in Benin City

Location of Automobile workshop	CD	PLI
NW	4265.71	331.08
NE	4348.90	313.12
SW	3843.91	287.54
SE	3639.84	313.86

The pollution load index values as calculated for automobile workshops in all zones were far greater than 1 (Table 11). This is an indication that the soil samples from all zones were severely polluted by the heavy metals.

4.0 Conclusion

The anthropogenic contamination status of soil from automobile workshops has been evaluated using various pollution indices and the results are in agreement in suggesting that the test soil samples are severely contaminated by heavy metals; and that automobile workshops are active point-sources for the dispersal of heavy metals into soil in Benin City.

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